

# Dielectric relaxation of non-conducting colloidal particles in non-binary solutions: mutual enhancement of adsorption oscillations

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## Abstract

This paper deals with the low-frequency dielectric dispersion (LFDD) of colloidal suspensions with non-binary electrolyte solutions as dispersion media. Starting from the theory of double-layer concentration polarization in AC fields, it is demonstrated that counterions can undergo significant adsorption oscillations which can increase to a large extent the dielectric increment of the suspensions. It is also shown that such oscillations can also affect the characteristic relaxation frequency of the dielectric spectrum,  $\omega_{cr}$ . This quantity can be either larger or smaller than it would be in a purely binary electrolyte, in which adsorption oscillations do not occur. The predictions of the theory are compared to experimental LFDD data reported in the literature. © 1997 Elsevier Science B.V.

**Keywords:** Adsorption oscillations; Concentration polarization of the Stern layer; Low frequency dielectric dispersion; Non-binary electrolytes

## 1. Introduction

The experimental study of the low-frequency dielectric dispersion (LFDD) of a suspension of colloidal particles has been shown to be a very significant tool in the characterization of their double-layer properties. Since the interpretation of the relevant experimental data is based on a theoretical model of the mechanisms of double-layer polarization in AC fields, it is important that the model takes into account all the essential features of the problem.

It is usual that the dispersion media chosen to

perform dielectric measurements in colloidal systems consist of aqueous solutions of binary electrolytes. In the framework of such studies, the effect of additional ions (e.g.  $H^+$  or  $OH^-$ ) is underestimated, and they are only considered in the calculation of quantitative parameters of the system, such as the zeta or Stern potentials of the interface.

This binary-electrolyte approach is often employed even in suspensions with essentially non-binary dispersion media (for instance, natural disperse systems, or suspensions of biological cells). In these and other cases the application of the approximate treatment considering only one type of cation and one type of anion is not justified. Although the contribution of the admixture (additional) ions to the bulk conductivity  $K_0$  might be negligibly small, they can exhibit high

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adsorbability in the double layer (DL). If the motion of such ions involves a substantial part of the net charge transfer within the DL, or between this and the bulk solution, the approximation of the binary electrolyte is not valid, and the dispersion medium must be regarded as multi-ion solution.

Some important features of the polarization of the DL in multi-ion media have been discussed in Refs. [1,2]. However, attention was only focussed on the ions which contribute significantly to  $K_0$  and/or provide electroneutrality to the bulk solution. Their possible extra-adsorption at the DL was not considered in those papers. The problem was considered later in Ref. [3], where it was shown that mutual enhancement of ordinary and additional counterion-adsorption oscillations can occur. The effect of this phenomenon on the low-frequency limit of the dielectric increment of a colloidal suspension,  $\Delta\epsilon'_r(0)$ , was analyzed in that article, whereas the frequency dependence of  $\Delta\epsilon'_r$  was studied in Ref. [4], for the simple case that the mobility of the additional counterion is equal to that of the counterion of the binary supporting solution. It was found that the enhancement of adsorption oscillations had some effect on the characteristic relaxation frequency  $\omega_{cr}$  of the LFDD spectrum of a colloidal suspension.

A simple qualitative account of the phenomenon can be given as follows. Let us focus, for example, in the universal presence of  $H^+$  and  $OH^-$  ions in aqueous electrolyte solutions. At least one of these two ions must have an extremely low concentration ( $\leq 10^{-7} \text{ mol l}^{-1}$ ), and, in fact, in a wide pH range ( $4 \leq \text{pH} \leq 10$ , say) for electrolyte concentrations of the order of  $10^{-3}$ – $10^{-2} \text{ M}$ , both of them will have comparatively low concentrations. They can thus be considered as “additional” ions in the context of the present article. Although their contribution to the volume conductivity of the dispersion medium is negligible because of their low concentrations, they can affect equilibrium electrosurface phenomena due to their adsorption at the inner part of the double layer. Under the action of an externally applied field, Stern-layer polarization will occur as a consequence of the tangential motion of adsorbed ions parallel to the particle surface; but, furthermore, the additional

ions can also be exchanged, perpendicularly to the surface, with other ions in the diffuse double layer. It is the analysis of the latter phenomenon and its effect on the dielectric constant of the suspension which is our aim in this paper.

According to classical explanations of the LFDD of suspensions, upon applying an electric field both the diffuse (or Gouy) layer and the part of the Stern layer where free exchange of ions with the diffuse layer occurs can become polarized. Due to ion exchange with the electrolyte solution outside the double layer, the latter maintains its quasi-equilibrium structure even after polarization and, as a consequence, changes take place in the concentration of the neutral electrolyte solution in contact with the double layer. This phenomenon, widely known as “concentration polarization”, brings about a diffusion of counterions which limits the electromigration fluxes started by the applied electric field. The larger the diffusion fluxes, the lower the amplitude of the dielectric dispersion.

Now, the action of a sinusoidally varying field will give rise to oscillations in the amounts of counterions adsorbed in both the inner and diffuse layers. Since electroneutrality is admitted everywhere due to the quasi-equilibrium conditions mentioned, the small amount of co-ion adsorption oscillations must be compensated for by a similarly small amount of counterion adsorption oscillations. But, these small oscillations can be attained by large opposite oscillations of the two types of counterions, i.e. those of the supporting electrolyte and the additional ones, like  $H^+$  or  $OH^-$ . Hence, the diffusion flux of one of the counterions will be decreased, whereas the other will increase, but to a different extent. As a consequence, the total diffusion contribution of counterion fluxes in the double layer will be lower, and the dielectric increment of the suspension will be larger.

In this work, a general treatment of the phenomenon will be given based on the previous particular cases analyzed in Refs. [3,4]. The paper is organized as follows: the general features of DL polarization in AC fields will be considered in Section 2. The consequences of these phenomena on the LFDD of a colloidal suspension are discussed in Section 3, and finally, Section 4 is devoted to the



analysis of a number of experimental works in the framework of the theory presented.

## 2. Concentration polarization of the DL in a non-binary electrolyte

### 2.1. Starting equations and boundary conditions

The concentration polarization theory of the DL was first developed in Ref. [5] for the case of a binary electrolyte, although the basic equations and approaches formulated in that work are independent of the number of ionic species in the dispersion medium.

Let us consider a colloidal suspension of non-conducting spheres of radius  $a$  with a dispersion medium consisting of an electrolyte solution with  $N$  ionic species of valencies  $z_i$  and equilibrium concentrations  $c_i^0$  ( $i=1, \dots, N$ ). In the presence of a variable electric field, the concentration of ions will be given by:

$$c_i(\mathbf{r}, t) = c_i^0(\mathbf{r}) + \delta c_i(\mathbf{r}, t) \quad (1)$$

where  $\mathbf{r}$  is the position vector with origin in the centre of the particle, and  $\delta c_i$  represents the effect on the concentration of species  $i$  in the bulk electrolyte of the double-layer deformation by the applied field (concentration polarization). If the diffusion coefficients of the ions in the solution are denoted by  $D_i$  ( $i=1, \dots, N$ ), the expressions for  $\delta c_i$  are [1]:

$$\begin{aligned} \partial_t \delta c_i - D_i \nabla^2 \delta c_i + z_i D_i c_i^0 \\ \times \frac{\sum_{j=1}^{N-1} (D_j - D_N) z_j \nabla^2 \delta c_j}{\sum_{j=1}^{N-1} (z_j D_j - z_N D_N) c_j^0} = 0, \\ i = 1, \dots, N-1 \end{aligned} \quad (2)$$

It is further assumed that the applied field strength is small enough to ensure local electrical neutrality in the electrolyte:

$$\sum_{j=1}^N z_j \delta c_j = 0 \quad (3)$$

which is analogous to the condition of local

electrical neutrality in the absence of the field:

$$\sum_{j=1}^N z_j c_j^0 = 0 \quad (4)$$

The equation for the perturbation electric potential  $\psi$ , (in dimensionless form  $y = e\psi/kT$ ) is given by [1]:

$$\nabla^2 y = - \frac{\sum_{j=1}^{N-1} (D_j - D_N) z_j \nabla^2 \delta c_j}{\sum_{j=1}^{N-1} (z_j D_j - z_N D_N) c_j^0} \quad (5)$$

In order to obtain an analytical solution to the problem of potential and concentration distributions, it is first necessary to separate and solve the coupled equations (Eq. (2)). The separation is immediate only if (1) a binary electrolyte is considered ( $N=2$ ; there will then be only one Eq. (2)), and (2) if all ions have equal mobilities ( $D_1 = D_2 = \dots = D_N$ ).

The general solution to Eqs. (2)–(5) in the case of an alternating electric field of frequency  $\omega$  has been given by Hinch et al. [6]. A more simple procedure was described independently in Ref. [2], where it was demonstrated that the solution involves finding the roots of an  $(N-1)$ th degree polynomial with real coefficients. However, the general solution of Eq. (2) is rather cumbersome, thus making the derivation of expressions for LFDD very complicated. Therefore, we will reach a reasonable compromise: it will be assumed that the electrolyte contains three univalent species, two of which have similar diffusion coefficients:

$$z_1 = z_2 = -z_3 = \pm 1, \quad D_2 \approx D_3 = D \quad (6)$$

( $D_1$  is arbitrary and might be very different to  $D$ : this is the case, for instance, of a KCl solution with  $H^+$  or  $OH^-$  additional ions).

The conditions in Eq. (6) allow us to obtain the following expressions:

$$\begin{aligned} \psi = \left[ -E \left( r + \frac{a^3}{2r^2} \right) + \frac{d_\phi}{r^2} \right] \cos \theta e^{i\omega t} \\ + \frac{kt}{e} \frac{(D - D_1) \delta c_1}{2c_3^0 D + (D_1 - D) c_1^0} \end{aligned} \quad (7)$$

$$\delta c_1 = d_1 \frac{a^2}{r^2} \left[ 1 + (1+i) \frac{r}{r_1} \right] \cos \theta e^{i\omega t} e^{-(1+i)r/r_1} \quad (8)$$

$$\delta c_2 = d_2 \frac{a^2}{r^2} \left[ 1 + (1+i) \frac{r}{r_2} \right] \cos(\theta) e^{i\omega t} \times e^{-(1+i)r/r_2} - \frac{c_2^0 \delta c_1}{c_3^0 + c_2^0} \quad (9)$$

where  $i = \sqrt{-1}$ ,  $\theta$  is the angle between the radius vector  $r$  and the applied field  $E$  (modulus  $E$ ), and  $r = |r|$ . The quantities  $r_i$  are given by:

$$r_i^2 = \frac{2D_{\text{ef},i}}{\omega} \quad (10)$$

where  $D_{\text{ef},i}$ , the effective diffusion coefficients of the electrolyte, are given by:

$$D_{\text{ef},1} = \frac{D_1}{1 + c_1^0(D_1 - D)/2c_3^0 D}, \quad D_{\text{ef},2} = D \quad (11)$$

Note that  $\delta c_3 = \delta c_1 + \delta c_2$ , according to Eq. (3) and Eq. (6). In Eqs. (7)–(9), the unknowns  $d_\phi$ ,  $d_1$ ,  $d_2$  can be obtained by substitution of the solutions of Eqs. (7)–(9) into the boundary conditions of the problem. For a thin double layer ( $\kappa a \gg 1$ , with  $\kappa$  the reciprocal Debye length), these conditions are [5]:

$$\frac{\partial \Gamma_j}{\partial t} + J_j|_{r=a} + \nabla_s \cdot I_j = 0, \quad j = 1, 2, 3 \quad (12)$$

here  $J_j|_{r=a}$  is the normal flux of ions of type  $j$  from the bulk of the dispersion medium to the particle surface:

$$J_j|_{r=a} = -D_j [\partial \delta c_j / \partial r + z_j c_j^0 \partial y / \partial r]_{r=a} \quad (13)$$

In Eq. (12),  $\Gamma_j$  is the adsorption density of the species  $j$ , and  $I_j$  is the tangential flux of ions in the quasi-equilibrium part of the double layer, i.e. the region which retains its quasi-equilibrium structure (even in the presence of the external field) due to efficient ion exchange with the dispersion medium. This region includes the diffuse or Gouy layer and that part of the Stern layer where free exchange of ions with the diffuse part is possible. If the mean residence time  $\tau_{\text{res}}$  of adsorbed ions is small, i.e. if

$$\omega \tau_{\text{res}} \ll 1 \quad (14)$$

then the polarized Stern layer can retain its quasi-equilibrium structure. The problem can be further

simplified if we confine ourselves to the case of strongly charged particles, for which the equilibrium Stern potential  $\psi_0$  satisfies:

$$|\psi_0| \geq 100 \text{ mV} \quad (15)$$

as in that case, the adsorption and tangential fluxes of co-ions can be neglected:

$$J_j|_{r=a} = 0 \quad \text{for} \quad z_j \psi_0 > 0 \quad (16)$$

Expressions for the surface divergence of the tangential flux of counterions can then be written as [7]:

$$\nabla_s \cdot I_j = - \frac{D_j R_j}{a \sin \theta} \frac{\partial}{\partial \theta} \times \left[ \sin \theta \left( \frac{\partial \delta c_j}{\partial \theta} + z_j c_j^0 \frac{\partial y}{\partial \theta} \right)_{r=a} \right], \quad z_j \psi_0 < 0 \quad (17)$$

where  $R_j$ , the generalized relaxation parameter, has three contributions corresponding, respectively, to electromigrational and diffusive fluxes of counterions in the diffuse ( $R_j^d$ ) or Stern ( $R_j^b$ ) layers, and to electroosmotic transfer in the diffuse layer ( $R_j^v$ ). They can be calculated from:

$$R_j = R_j^d + R_j^b + R_j^v \quad z_j \psi_0 < 0 \quad (18)$$

$$R_j^d = \frac{\Gamma_{dj}^0}{a c_j^0} \quad R_j^b = \frac{D_j^b \Gamma_{bj}^0}{a D_j c_j^0} \quad (19)$$

$$R_j^v = \frac{6m_j}{\kappa a} \left[ e^{\tilde{\zeta}/2} - 1 - 2 \ln \left( \frac{1 + e^{\tilde{\zeta}/2}}{2} \right) \right]$$

Here,  $\Gamma_{dj}^0$  ( $\Gamma_{bj}^0$ ) is the equilibrium adsorption density of counterion  $j$  in the diffuse (quasi-equilibrium Stern) layer,  $D_j^b$  is the lateral diffusion coefficient of species  $j$  in the quasi-equilibrium Stern layer,  $\tilde{\zeta}$  is the dimensionless zeta potential of the particles ( $\tilde{\zeta} = e\zeta/kT$ ), and  $m_j$  is the dimensionless parameter:

$$m_j = \frac{2\epsilon'_{rd} \epsilon_0 k^2 T^2}{3\eta e^2 D_j} \quad (20)$$

$\epsilon'_{rd}$  being the dielectric constant of the dispersion medium,  $\eta$  its viscosity, and  $\epsilon_0$  the permittivity of



vacuum. In the polarized double layer,

$$\Gamma_j = \Gamma_{dj} + \Gamma_{bj} = \Gamma_{dj}^0 + \delta\Gamma_{dj} + \Gamma_{bj}^0 + \delta\Gamma_{bj} = \Gamma_j^0 + \delta\Gamma_j \quad (21)$$

and the adsorption oscillation can be expressed as:

$$\frac{\partial\Gamma_j}{\partial t} = \frac{\partial\delta\Gamma_j}{\partial t} = i\omega\delta\Gamma_j \quad (22)$$

in an alternating field of frequency  $\omega$ .

## 2.2. Adsorption oscillations in a non-binary electrolyte

The condition of local electroneutrality should be fulfilled for each part of the double layer. If the quasi-equilibrium nature of the concentration polarization mechanism prevails, we can write this condition in the form:

$$\sum_{j=1}^N z_j \delta\Gamma_j = 0 \quad (23)$$

because the polarization of the bulk by a strongly charged, non-conducting particle is negligible [5].

From Eq. (23) for a binary electrolyte, the polarization contribution is as low for counterion adsorption as for co-ion adsorption, and both will be negligible. Calculations reported in Ref. [5] support the conclusion that the influence of adsorption oscillations on LFDD is negligibly small. However, in the case of three ions (two counterions,  $j=1, 2$ , and one co-ion,  $j=3$ ), Eq. (23) takes the form:

$$\delta\Gamma_1 + \delta\Gamma_2 = \delta\Gamma_3 \approx 0 \quad (24)$$

Note that Eq. (24) means that it is the *sum* of polarization contributions to counterion adsorption which must be very small, and not both separately. It may thus happen that adsorption oscillations of counterions at the quasi-equilibrium part of the double layer are significant; we call this phenomenon the mutual enhancement of adsorption oscillations. Note that polarization contributions to adsorption enter the boundary conditions (Eq. (12) separately.

In most cases of practical importance, the expressions for adsorption oscillations of counter-

ions can be represented as (see Appendix A):

$$\begin{aligned} \frac{d\Gamma_j}{dt} = i\omega\delta\Gamma_j = i\omega(-1)^j \frac{aR_F}{c_3^0} \\ \times (c_1^0\delta c_2 - c_2^0\delta c_1)_{r=a} \quad j=1, 2 \end{aligned} \quad (25)$$

where

$$R_F = R_d/2 + \frac{(G_1 + R_d/2)(G_2 + R_d/2)}{R_d/2 + (c_1^0 G_1 + c_2^0 G_2)/c_3^0} + \gamma \geq 0 \quad (26)$$

and

$$R_d = \frac{\Gamma_{dj}^0}{ac_j^0} = \frac{2[\exp(|y_0/2|) - 1]}{\kappa a} \quad (26a)$$

Expressions for  $G_{1,2}$  and  $\gamma$  depend on the characteristics of counterion adsorption in the Stern layer. Some simple examples are given below (see also Appendix A).

If the adsorption of the two counterions is such that  $\Gamma_{bj}^0$  is proportional to  $c_j^0 \exp(|y_0|/2)$  (unsaturated adsorption), then

$$G_{1,2} = \frac{\Gamma_{b1,2}^0}{ac_{1,2}^0} \quad \gamma = 0 \quad (27)$$

If the situation is such that the counterions 1, 2 adsorb on different sites, according to the Stern adsorption isotherm:

$$\Gamma_{bj}^0 = \frac{N_j^s}{N_A} \frac{(c_j^0/c_j^b) e^{|y_0|}}{1 + (c_j^0/c_j^b) e^{|y_0|}} \quad j=1, 2 \quad (28)$$

where  $N_j^s$  is the surface density of adsorption sites for the  $j$ th ion,  $N_A$  is the Avogadro number, and the constant  $c_j^b$  is determined by the specific adsorption potential. From this [3]:

$$G_{1,2} = \frac{\Gamma_{b1,2}^0/ac_{1,2}^0}{1 + (c_{1,2}^0/c_{1,2}^b) e^{|y_0|}} \quad \gamma = 0 \quad (28a)$$

$\gamma$  is not zero if both counterions can adsorb on the same sites (density  $N_s$ ):

$$\Gamma_{bj}^0 = \frac{N_s}{N_A} \frac{(c_j^0/c_j^b) e^{|y_0|}}{1 + (c_1^0/c_1^b + c_2^0/c_2^b) e^{|y_0|}} \quad j=1, 2 \quad (29)$$

and

$$G_{1,2} = \frac{\Gamma_{b1,2}^0 / ac_{1,2}^0}{1 + (c_1^0/c_1^b + c_2^0/c_2^b) e^{|y_0|}}$$

$$\gamma = \frac{c_3^0}{c_1^b} G_2 e^{|y_0|} = \frac{c_3^0}{c_2^b} G_1 e^{|y_0|} \quad (29a)$$

Finally, if only one of the ions can adsorb (species 1, for instance), either Eq. (28) or Eq. (29) can be used, setting the other  $c_j^b$  parameter equal to infinite ( $c_2^b \rightarrow \infty$ ).

$R_F$  is an important parameter of the model, and it might be worthwhile to consider its physical meaning. Let us note that  $R_F$  may be large when both counterions can easily adsorb at the Stern layer ( $G_1, G_2 \gg 1$ ). Since the time variation of the adsorbed amount of any of the counterions is directly proportional to  $R_F$  (cf. Eq. (25), high values of  $R_F$  mean a large adsorption oscillation effect, provided  $(c_1^0 \delta c_2 - c_2^0 \delta c_1) \neq 0$ . Note that while for a binary electrolyte this difference is always identical to zero, in the three-ion solution it is different from zero, as long as the relaxation parameters  $R_1$  and  $R_2$  (Eq. (18) and Eq. (19) are different, as expected in the case of  $H^+$  or  $OH^-$  as additional counterion.

### 3. Adsorption oscillations and LFDD

If  $\epsilon_r'(\omega)$  denotes the dielectric constant of a suspension with solids volume fraction  $\phi$ , in the case of dilute suspensions a linear relationship is found between  $\epsilon_r'(\omega)$  and  $\phi$ :

$$\epsilon_r'(\omega) = \epsilon_{rd}' + \phi \Delta \epsilon_r'(\omega) \quad (30)$$

where  $\epsilon_{rd}'$  is the dielectric constant of the dispersion medium, and  $\Delta \epsilon_r'(\omega)$  is the so-called dielectric increment, containing the effect of the particles and their double layers on the overall dielectric behaviour of the system. In the concentration polarization approximation for thin double layers, it can be shown from Eq. (II.31) of Ref. [5] that:

$$\Delta \epsilon_r'(\omega) = \frac{3}{2} \epsilon_{rd}' (\kappa a)^2 \frac{2c_3^0 - c_1^0 + D_1 c_1^0 / D}{2c_3^0} \frac{1}{W_2^2} \frac{\text{Im}(d_\phi)}{a^3 E} \quad (31)$$

where  $d_\phi$  is the induced dipole coefficient of the colloidal particle (cf. Eq. (7), and

$$W_j^2 = \frac{a^2}{2D_{ef,j}} \omega \quad (32)$$

The expression for  $d_\phi$  is hence the essential step in the determination of  $\Delta \epsilon_r'(\omega)$ . Substitution of Eqs. (7)–(9) into the expressions for the fluxes and into Eq. (25) makes it possible to express fluxes and adsorption oscillations in terms of the unknowns  $d_\phi$ ,  $d_1$  and  $d_2$ . Further substitution of the expressions obtained into boundary conditions (Eq. (12) for counterions ( $j=1, 2$ ), and Eq. (16) for co-ions ( $j=3$ ) leads to a set of three algebraic equations:

$$A_{j1}x_1 + A_{j2}x_2 + A_{j3}d_\phi = (3/2)A_{j4}a^3E \quad j=1, 2, 3 \quad (33)$$

with

$$A_{11} = (1 + R_1 + f_1 + iW_1^2 R_F)c_2^0 + (1 + R_2 + f_2 + iW_2^2 R_F)c_1^0 + \frac{c_1^0 c_2^0}{c_2^0 + c_3^0} [f_1 - f_2 - i(W_1^2 - W_2^2)R_F] \quad (34)$$

$$A_{12} = \frac{c_1^0 c_2^0}{c_3^0} \left( R_1 - R_2 + \frac{2c_3^0}{c_2^0 + c_3^0} \times [f_1 - f_2 + i(W_1^2 - W_2^2)R_F] \right) \quad (35)$$

$$A_{13} = c_1^0 c_2^0 \left[ \frac{D_1}{D} (1 + R_1) - 1 - R_2 \right] \quad (36)$$

$$A_{14} = c_1^0 c_2^0 \left( \frac{D_1 R_1}{D} - R_2 \right) \quad (37)$$

$$A_{21} = R_1 - R_2 \quad (38)$$

$$A_{22} = \frac{c_1^0 R_1 + c_2^0 R_2}{c_3^0} \quad (39)$$

$$A_{23} = c_3^0 + c_2^0(1 + R_2) + \frac{D_1}{D} c_1^0(1 + R_1) \quad (40)$$

$$A_{24} = c_2^0 R_2 + \frac{D_1}{D} c_1^0 R_1 \quad (41)$$



$$A_{31} = c_3^0 \frac{f_1 - f_2}{c_2^0 + c_3^0} \quad (42)$$

$$A_{32} = 1 + \frac{c_1^0 f_1 + c_2^0 f_2}{c_3^0} - \frac{c_1^0 c_2^0 (f_1 - f_2)}{c_3^0 (c_2^0 + c_3^0)} \quad (43)$$

$$A_{33} = -c_3^0 \quad A_{34} = 0 \quad (44)$$

$$x_1 = \frac{a^2 kT}{z_1 e \cos \theta e^{i\omega t}} \left[ \frac{c_2^0 \delta c_1 - c_1^0 \delta c_2}{c_3^0} + \frac{D_{ef1} - D}{D} \frac{2c_2^0}{c_2^0 + c_3^0} \delta c_1 \right]_{r=a} \quad (45)$$

$$x_2 = \frac{a^2 kT}{z_2 e \cos \theta e^{i\omega t}} \left[ \delta c_1 + \delta c_2 + \frac{D_{ef1} - D}{D} \frac{c_3^0}{c_2^0 + c_3^0} \delta c_1 \right]_{r=a} \quad (46)$$

and

$$f_j = \frac{iW_j^2}{1 + (1+i)W_j}$$

Solving Eq. (33) for  $d_\phi$  allows one to obtain the desired expression for  $\Delta\epsilon_r'(\omega)$  and  $\Delta\epsilon_r'(0)$ . In particular, it can be shown that [3]:

$$\Delta\epsilon_r'(0) = \frac{9}{16} \epsilon_{rd}'(\kappa a)^2 \left[ \left( \frac{c_2^0}{c_3^0} \frac{R_2}{1+R_2} + \frac{c_1^0}{c_3^0} \frac{R_1}{1+R_1} \right)^2 + 2 \frac{c_1^0 c_2^0}{(c_3^0)^2} \frac{(R_1 - R_2)^2 (1+R_F)}{(1+R_1)^2 (1+R_2)^2} \right] \quad (47)$$

Note that the presence of  $R_F$  (cf. Eq. (26) in Eq. (47) demonstrates that  $\Delta\epsilon_r'(0)$  depends on the characteristics of the adsorption oscillation effect. Furthermore, the sign of  $R_F$  implies a positive contribution to  $\Delta\epsilon_r'(0)$ . From the dependence of  $\Delta\epsilon_r'(0)$  on  $c_j^0$  and  $R_j$ , the conditions for a significant influence of the oscillation on  $\Delta\epsilon_r'(0)$  can be summarized as follows:

- (1) If either  $c_1^0 c_2^0 = 0$ , or species 1 and 2 have identical valencies, diffusion coefficients, etc., the electrolyte is binary and adsorption oscillations will not be present.
- (2) If  $c_1^0 c_2^0 \neq 0$ , and  $R_1 \approx R_2$ ,  $\Delta\epsilon_r'(0)$  will be little affected by the oscillations.
- (3) If  $c_1^0 c_2^0 \neq 0$ , and  $R_1 \neq R_2$ , the enhancement is

possible, and will be more important the larger the difference  $R_1 - R_2$ .

Eq. (47) also shows that in the case of a binary electrolyte [8]:

$$\Delta\epsilon_r'(0) \leq (\Delta\epsilon_r')_{\max} = \frac{9}{16} \epsilon_{rd}'(\kappa a)^2 \quad (48)$$

but in the three-ion case,  $\Delta\epsilon_r'(0)$  can be much higher than Eq. (48). This can be understood if some extreme conditions are assumed. Thus, the limiting value  $(\Delta\epsilon_r')_{\max}$  corresponds to a situation where the surface charge density  $\sigma_0$  tends to infinity. If, additionally, the Stern layer charge tends also to infinity ( $G_1, G_2 \rightarrow \infty$ ), but that of the diffuse layer remains finite ( $\psi_0$  finite), then  $\Delta\epsilon_r'(0) \rightarrow \infty$ , provided that  $c_1^0 c_2^0 (R_1 - R_2) \neq 0$ . Note that high values of  $G_1$  and  $G_2$  can be achieved for finite  $R_1$  and  $R_2$  if the physically reasonable assumption is made that the mobility of counterions at the Stern layer is low:

$$R_{1,2}^b \approx \frac{D_{1,2}^b G_{1,2}}{D} \quad \text{finite,}$$

$$\text{if } \frac{D_{1,2}^b}{D} \ll 1 \quad G_{1,2} \gg 1$$

Hence:

$$\Delta\epsilon_r'(0) > \frac{9}{16} \epsilon_{rd}'(\kappa a)^2 2 \frac{c_1^0 c_2^0}{(c_3^0)^2} \frac{(R_1 - R_2)^2 R_F}{(1+R_1)^2 (1+R_2)^2} \quad (49)$$

if  $c_1^0 c_2^0 (R_1 - R_2) \neq 0$  and  $R_F \rightarrow \infty$ . In practice,  $G_1$  and  $G_2$  (and, as a consequence,  $R_F$ ) remain finite and so does  $\Delta\epsilon_r'(0)$ , but the extreme condition (Eq. (49) shows that  $\Delta\epsilon_r'(0)$  can reach extremely high values, even if the concentration of one of the counterions is very small (for instance,  $c_1^0 \ll c_2^0$ ). This is possible because their adsorption cannot be small. In Ref. [3] it has been shown that moderate and feasible adsorption conditions for both counterions led to significant dielectric enhancement, comparable to that found experimentally by different authors [9–16].

Another quantity of interest in the description of the LFDD of a colloidal system is the relaxation

or characteristic frequency  $\omega_{cr}$ , given by the condition:

$$\Delta\epsilon'_r(\omega_{cr}) = \frac{1}{2}\Delta\epsilon'_r(0) \quad (50)$$

From the numerical solution of Eq. (33), the whole dielectric spectrum can be obtained, and from this,  $\omega_{cr}$ . With the aim of analyzing the effect of adsorption oscillations on this quantity, let us consider the practical situation in which a small amount of ionic species 1 ( $c_1^0 \ll c_2^0$ ), for instance  $H^+$  or  $OH^-$ , is added to a KCl solution ( $D_{K^+} \approx D_{Cl^-}$ ). In such a case, a significant effect of that small amount (at constant equilibrium Stern potential) on LFDD is possible only because of the adsorption oscillation effect.

The following dimensionless quantities will be defined to measure the effect of adsorption oscillations on both  $\Delta\epsilon'_r(0)$  and  $\omega_{cr}$ :

$$X \equiv \frac{\Delta\epsilon'_r(0)}{\Delta\epsilon'_r(0)|_{c_1^0=0}} - 1 \quad (51)$$

$$Z \equiv \frac{\omega_{cr}}{\omega_{cr}|_{c_1^0=0}} \quad (52)$$

The total electrolyte concentration  $c_3^0$  and the relaxation parameter  $R_2$  will be kept constant. Strictly speaking, the  $X$  and  $Z$  values are influenced not only by adsorption oscillations, but also by the tangential transport of type-1 counterions along the DL. However, the latter effect is usually small. Therefore,  $X$  and  $Z$  accurately represent the contribution of adsorption oscillations to the low-frequency limit of the dielectric constant and to the critical frequency, respectively. Note that  $X > 0$  means a dielectric enhancement by the mechanism we are discussing, whereas  $Z \neq 1$  indicates an effect on the critical frequency. The behaviour of  $X$  is shown in Fig. 1. As observed, except when  $R_1 = R_2$ , the effect of adsorption oscillations is always positive, i.e. the dielectric increment is higher than would be obtained in the absence of the additional ion. The enhancement is more significant the larger  $R_f$  is.

The variation of the critical frequency with  $R_1$  for fixed  $R_2$  is shown in Figs. 2–4 for  $D_1 = D$ ,  $D_1 > D$  and  $D_1 < D$ , respectively. When  $D_1 = D$  (Fig. 2), the  $A_{31}$  coefficient of Eq. (33) will

be zero, and hence the adsorption oscillation will be present if  $A_{21} \neq 0$ , i.e. if  $R_1 \neq R_2$ , as is in fact demonstrated in Fig. 2. The behaviour if  $D_1 \neq D$  was expected to be different: in this case,  $A_{31}$  is non-zero and increases with frequency, but when  $\omega_{cr}$  is computed for  $D_1 > D$  (Fig. 3) or  $D_1 < D$  (Fig. 4) we again find that all curves intersect at the point  $R_1 = R_2$  and attain a value  $Z \approx 1$ . The small shifts of the intersection point towards the higher-frequency region ( $Z > 1$ ) for  $D_1 > D$  and towards lower critical frequencies ( $Z < 1$ ) for  $D_1 < D$  is related to the tangential transport of the minority ions (type-1 ions), and needs no special consideration here.

This behaviour is indicative of the fact that the coefficient  $A_{31}$  is small in the concentration polarization frequency range, this giving rise to a close relation between the effect of oscillations on  $\Delta\epsilon'_r(0)$  and  $\omega_{cr}$ . Such a relation is demonstrated if one considers that when  $X < 1$  (Fig. 1),  $Z \approx 1$  (Figs. 2–4).

Let us now consider the effect of adsorption oscillations (their magnitude is represented by  $R_f$ ) on  $\omega_{cr}$ . Figs. 5–7 show the results for  $D_1 = D$ ,  $D_1 > D$  and  $D_1 < D$ , respectively. For  $D_1 = D$  (Fig. 5)  $\omega_{cr}$  increases with  $R_f$  for small to moderate values of the latter quantity, and it decreases when  $R_f$  is increased further. This brings about a maximum in all the curves, except when  $R_1 \approx R_2$  (curve 2), when adsorption oscillations are negligibly small whatever the value of  $R_f$ .

For  $D_1 \neq D$ , the effective diffusion coefficient  $D_{ef1}$  (Eq. (11)) is of the order of  $D_1$  if  $c_1^0$  is small; one can expect that the values of  $\omega_{cr}$  for  $D_1 > D$  will be higher than those for  $D_1 = D$ , and the reverse will happen if  $D_1 < D$ . This is in fact demonstrated by the data in Figs. 6 and 7.

The characteristic frequency will be significantly different from the value corresponding to the binary electrolyte ( $Z$  very different from 1) if the effects of both  $D_{ef1}$  and  $R_f$  act in the same direction. For example, if  $D_1 > D$  and  $R_f$  takes moderate values (left-hand side of curves 3 and 4 in Fig. 6) a large increase in  $\omega_{cr}$  is found; for  $D_1 < D$  and high  $R_f$ ,  $\omega_{cr}$  shows an especially significant decrease (right-hand side of curves 1 and 3 in Fig. 7).



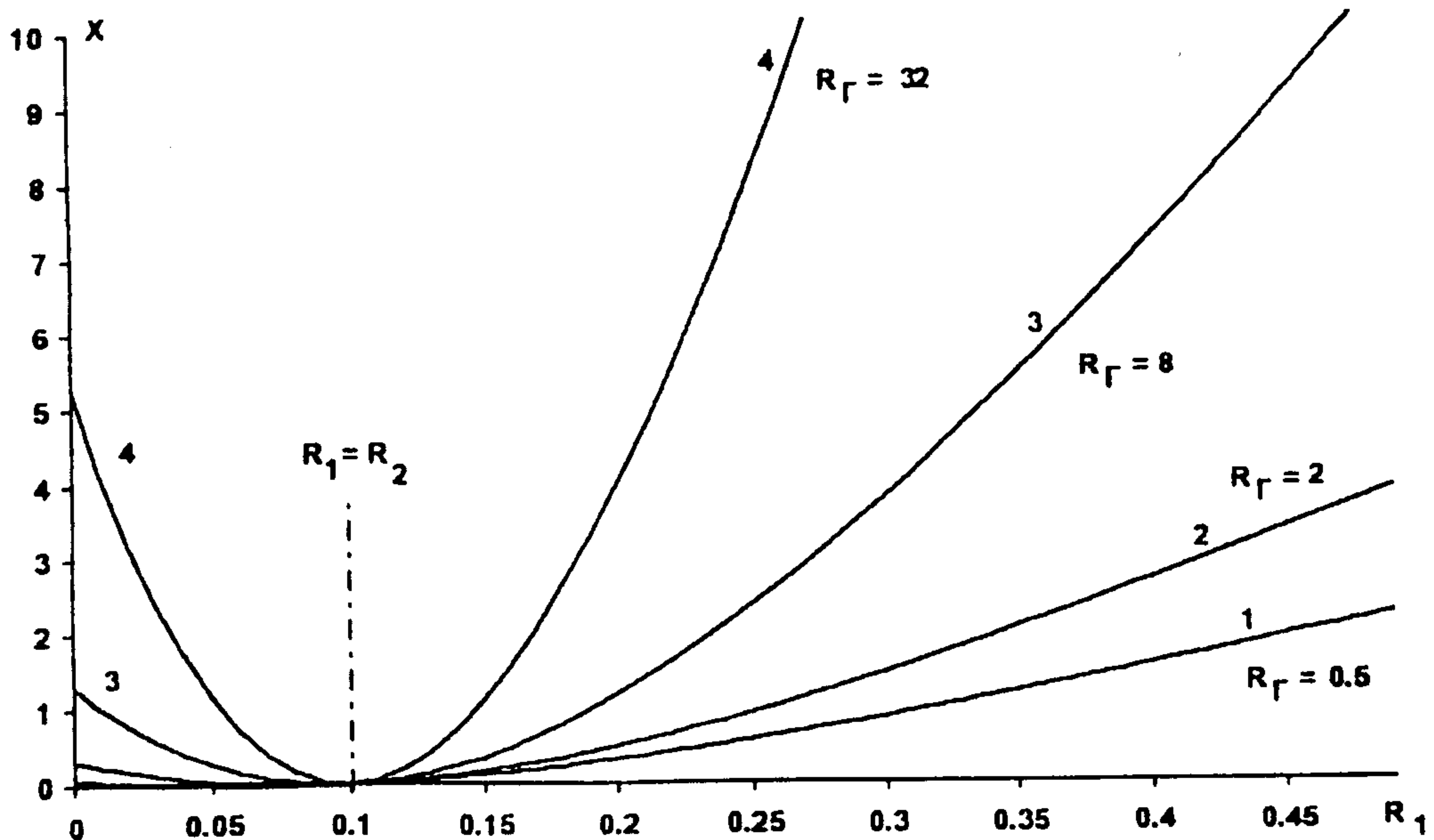


Fig. 1. Relative contribution of additional counterions (type 1) to the low-frequency limit of the dielectric increment (Eq. (51)) plotted as a function of the relaxation parameter  $R_1$  for  $R_2=0.1$ ,  $c_1^0/c_2^0=0.1$ , and different values of  $R_F$ . Curve 1:  $R_F=0.5$ ; curve 2:  $R_F=2$ ; curve 3:  $R_F=8$ ; curve 4:  $R_F=32$ .

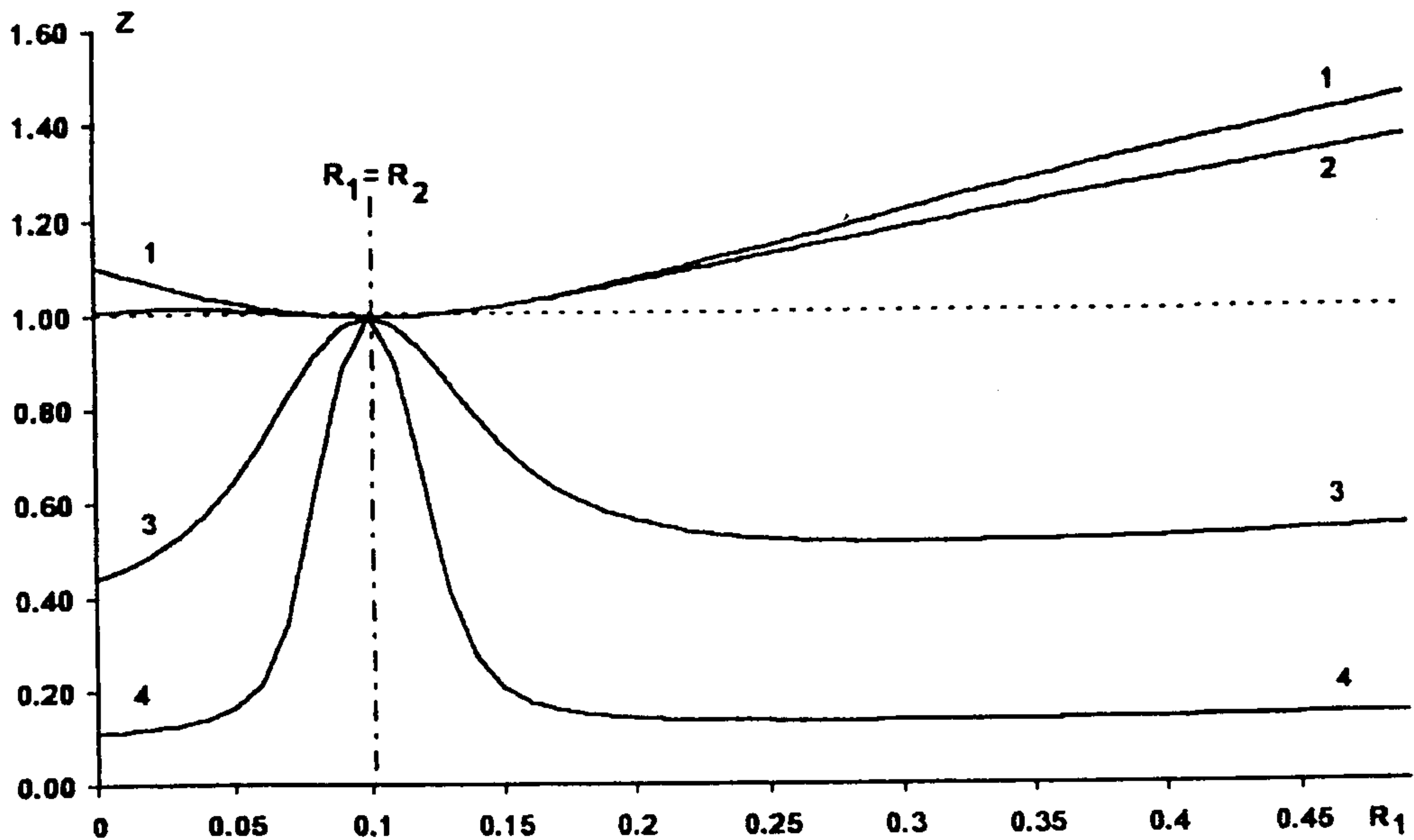
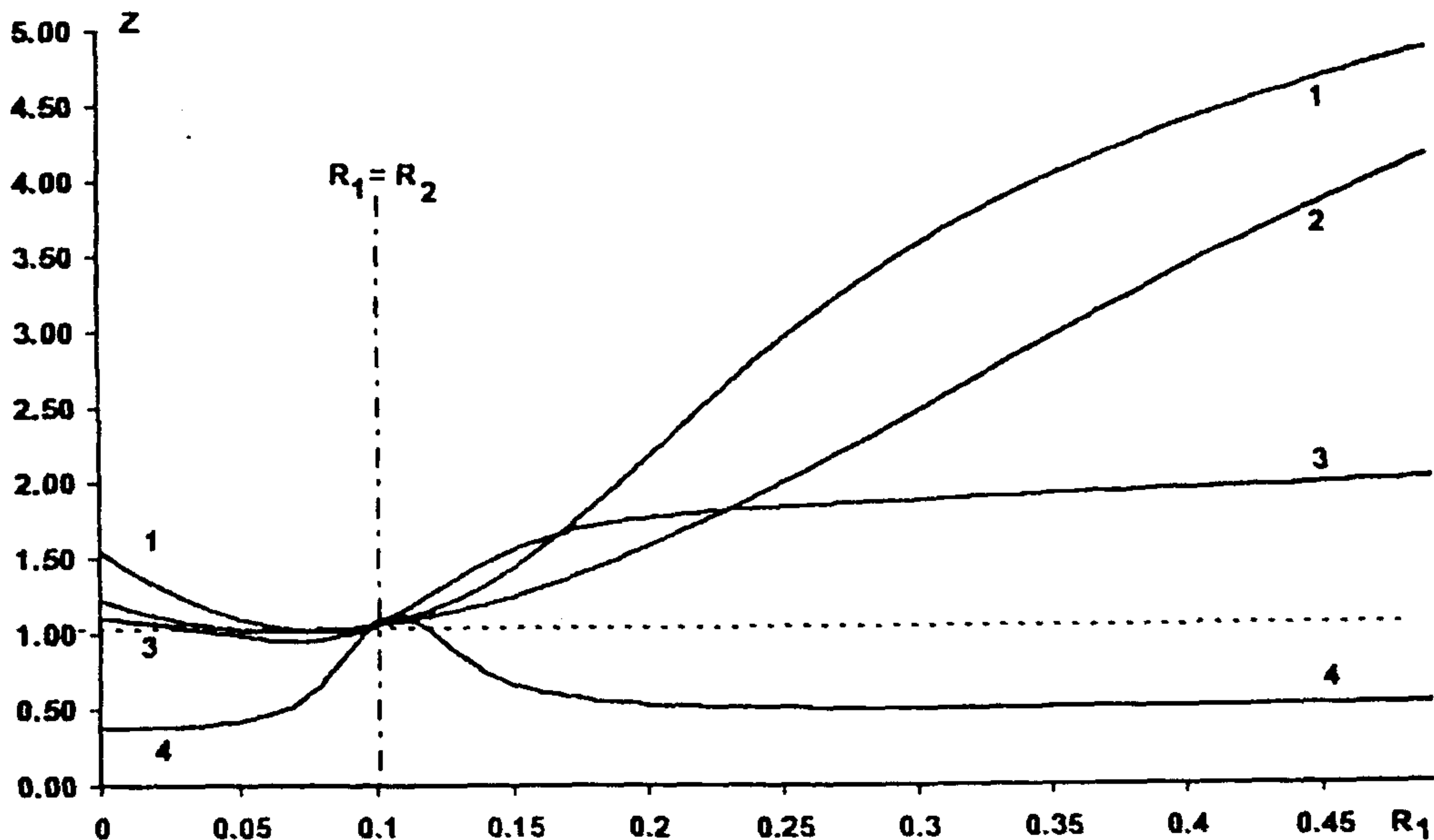
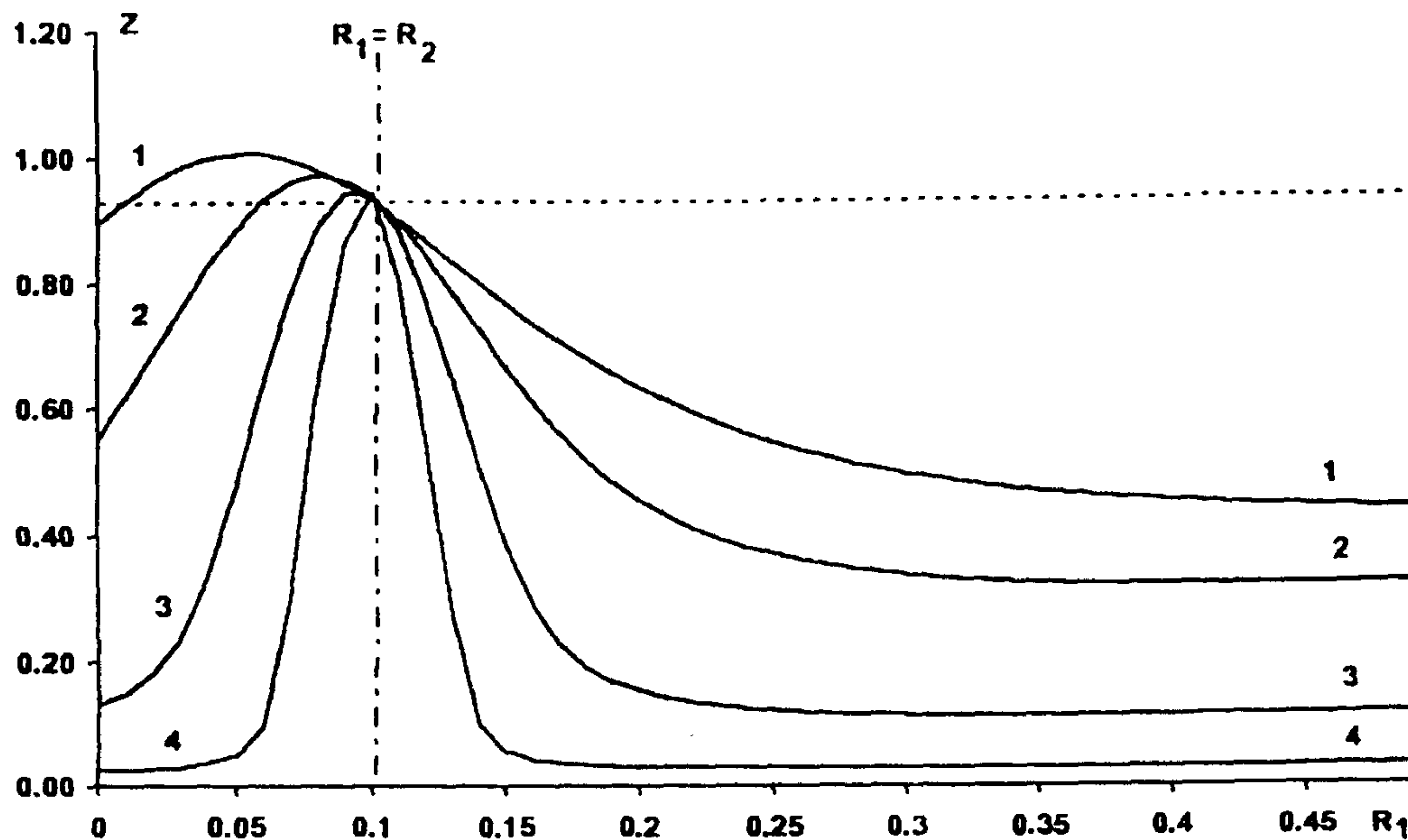


Fig. 2. Relative characteristic frequency (Eq. (52)) as a function of  $R_1$  for  $R_2=0.1$ ,  $c_1^0/c_2^0=0.1$ , and  $R_F$  as a parameter.  $D_1=D$ . Curve 1:  $R_F=0.5$ ; curve 2:  $R_F=2$ ; curve 3:  $R_F=8$ ; curve 4:  $R_F=32$ .

Fig. 3. As Fig. 2, but for  $D_1 = 5D$ .Fig. 4. As Fig. 2, but for  $D_1 = 0.2D$ .

#### 4. Comparison with experimental data

Grosse and Foster [9] summarized the experimental LFDD data obtained in a number of studies [10–14]. Such data can be easily compared

with the limitation given by Eq. (48), as done by Lyklema et al. [15] using the experimental data reported in Ref. [12]. As a whole, most experimental data on non-conducting particles clearly violate Eq. (48).



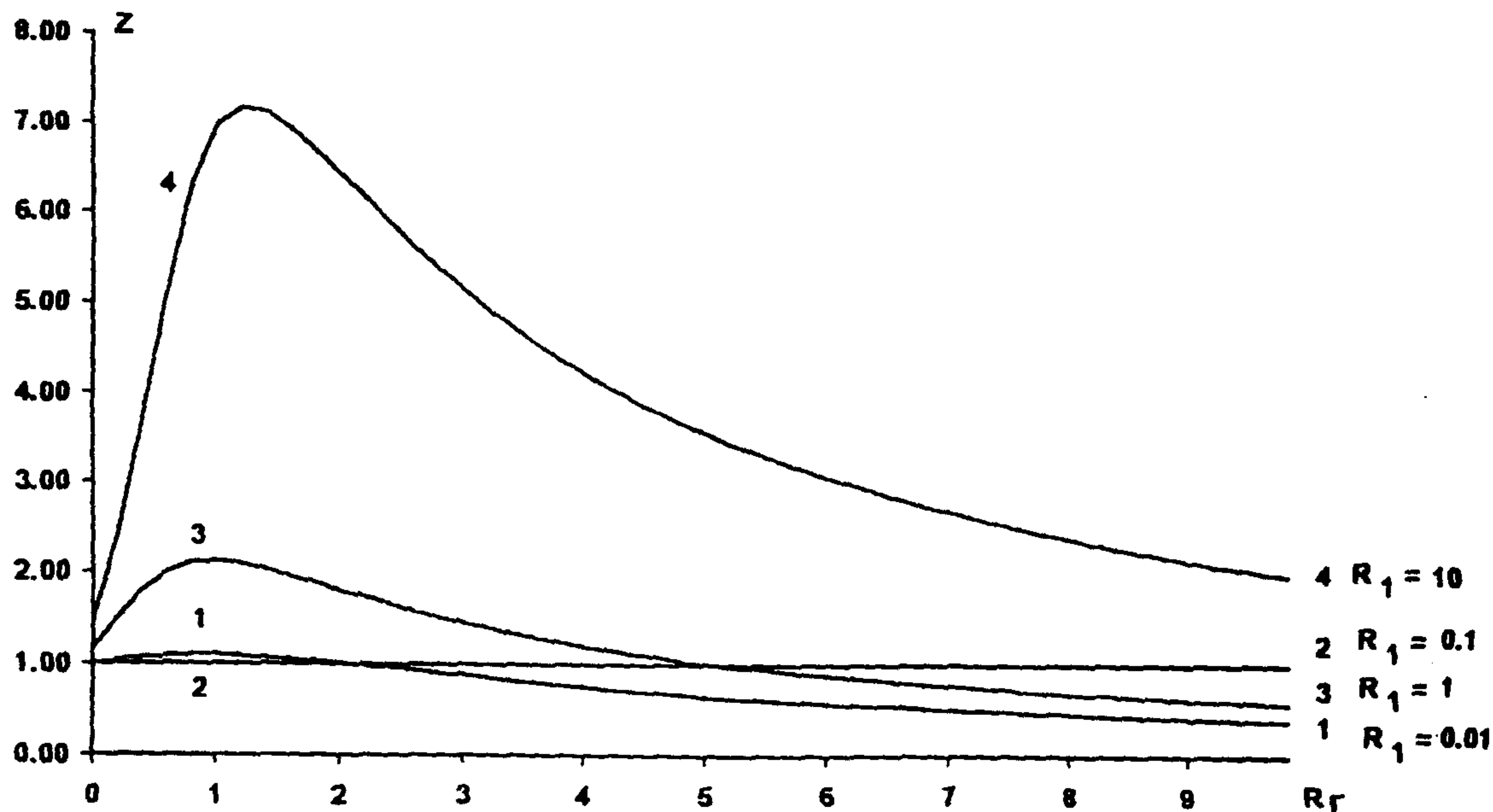


Fig. 5. Effect of the strength of the adsorption oscillations phenomenon (represented by  $R_f$ ) on the relative characteristic frequency, for  $R_2=0.1$  and  $c_1^0/c_2^0=0.1$ , with  $R_1$  as a parameter.  $D_1=D$ . Curve 1:  $R_1=0.001$ ; curve 2:  $R_1=0.01$ ; curve 3:  $R_1=0.1=R_2$ ; curve 4:  $R_1=10$ .

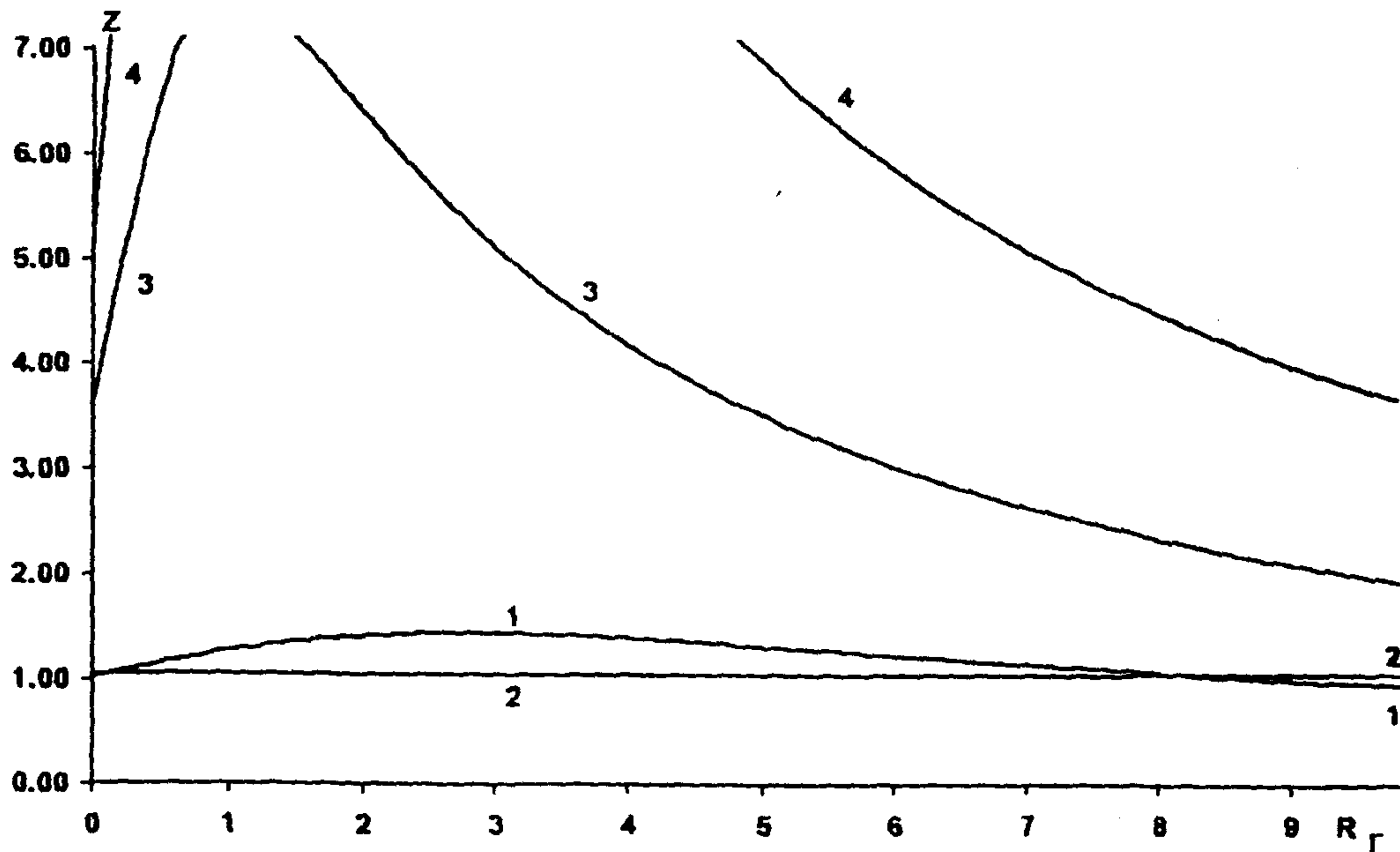
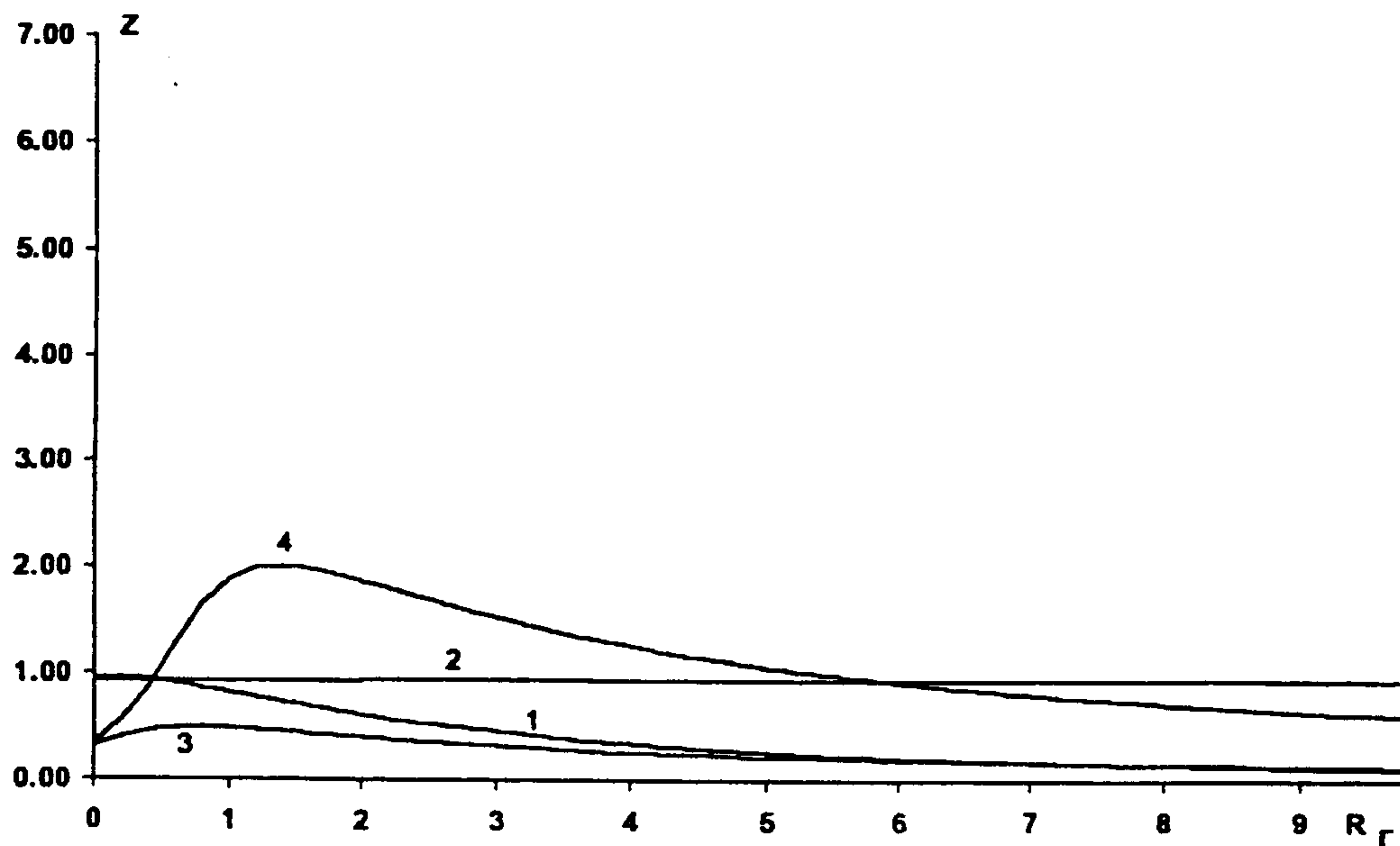


Fig. 6. As Fig. 5, but for  $D_1=5D$ .

Information concerning anomalously high values of dielectric increment is also presented in Ref. [16]. For a sufficiently low electrolyte concen-

tration ( $\leq 2 \times 10^{-4}$  M KCl) there is a clear indication that the theoretical maximum is surpassed, unlike data obtained at the high concentration

Fig. 7. As Fig. 5, but for  $D_1 = 0.2D$ .

range, where  $\Delta\epsilon'_r(0)$ , being anomalously high, remains below  $(\Delta\epsilon'_r)_{\max}$ .

Although the adsorption oscillations of counterions at the quasi-equilibrium double layer can be invoked to explain such anomalies, the possibility must be considered that there is aggregation between individual particles in the system [15]. In fact, this phenomenon may have a drastic effect on  $\Delta\epsilon'_r(0)$ , since  $d_\phi$  is roughly proportional to the particle or aggregate size. Such an increase in the dipole coefficient might well give rise to  $\Delta\epsilon'_r(0)$  above the value represented by the right-hand side of Eq. (48).

It is, however, possible to elucidate which of the two mechanisms (adsorption oscillations or aggregation) can be responsible for the high  $\Delta\epsilon'_r(0)$  values obtained; it suffices to check whether the increase in electrolyte concentration ( $c_3^0$ ) brings about higher or lower  $\Delta\epsilon'_r(0)/(\Delta\epsilon'_r)_{\max}$  ratios. If the mechanism responsible is aggregation, then the ratio should increase with concentration, since higher ionic strengths bring about more probable and faster aggregation processes, i.e., higher average values of  $d_\phi$  and hence of  $\Delta\epsilon'_r(0)$ . On the contrary, Eq. (47) shows that the relative contribution (always positive for  $\Delta\epsilon'_r(0)$ ) of adsorption

oscillations decreases with the increase of electrolyte concentration. Thus, in the case of the results reported by Springer et al. [12], it is shown that the ratio  $\Delta\epsilon'_r(0)/(\Delta\epsilon'_r)_{\max}$  decreases with concentration, and even Eq. (48) holds for the highest ionic strengths.

Nevertheless, the possibility of slight coagulation cannot be neglected in general, and both mechanisms can be working simultaneously. The mutual enhancement of counterion adsorption oscillations may explain the effect of  $c_3^0$  on  $\Delta\epsilon'_r(0)$ , whereas aggregation can account for the obtention of the extremely high values of this quantity.

Another test of the theory concerns the behaviour of the characteristic frequency  $\omega_{cr}$ . As discussed in the previous paragraph, the adsorption oscillations may shift  $\omega_{cr}$  to either higher or lower values, whereas coagulation of particles can only decrease  $\omega_{cr}$ . Therefore, the existence of anomalously high characteristic frequencies can be regarded as evidence of the predominating role of the adsorption oscillations mechanism. For example, the data presented in Ref. [16] show an increase of zeta potential with electrolyte concentration; therefore, one cannot ascribe the decrease of the  $\Delta\epsilon'_r(0)/[\Delta\epsilon'_r(0)]_{\max}$  ratio to the adsorption phenomenon.



## 5. Conclusion

We have analyzed the  $\omega_{cr}$  data of Ref. [16]. It is found that  $\omega_{cr}$  is about 2.5 times higher than the value corresponding to the binary electrolyte. Hence, it would be possible to explain the results of Ref. [16] consistently only in the framework of the mechanism described in this paper and in Ref. [3]: mutual enhancement of the adsorption oscillations of ordinary and additional counterions can lead to both anomalously high dielectric increments and high characteristic frequencies.

## Acknowledgment

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## Appendix A

### 7.1. Polarization contribution to counterion adsorption

Because of local equilibrium conditions in the polarized double layer, the polarization contributions to counterion adsorption can be related to the concentration increments near the external boundary of the double layer,  $(\delta c_j)_{r=a}$ , and to the increment of Stern potential  $\delta\psi$ :

$$\begin{aligned} \delta\Gamma_j &= (\Gamma_{dj}^0 + \Gamma_{bj}^0)_{\psi_0 + \delta\psi, c_i^0} + (\delta c_i)_{r=a} \quad i=1, 2, 3 \\ &- (\Gamma_{dj}^0 + \Gamma_{bj}^0)_{\psi_0, c_i^0} \quad i=1, 2, 3 \quad j=1, 2 \end{aligned} \quad (A.1)$$

or, after series expansion and neglecting quadratic

and higher terms in  $\delta\psi$ ,  $\delta c_j$ :

$$\begin{aligned} \delta\Gamma_j &= \left( \frac{\partial \Gamma_{dj}^0}{\partial \psi_0} + \frac{\partial \Gamma_{bj}^0}{\partial \psi_0} \right) \delta\psi \\ &+ \sum_{i=1}^3 \left( \frac{\partial \Gamma_{dj}^0}{\partial c_i^0} + \frac{\partial \Gamma_{bj}^0}{\partial c_i^0} \right) (\delta c_i)_{r=a} \quad j=1, 2 \end{aligned} \quad (A.2)$$

It is impossible to use Eq. (A.2) directly in the boundary conditions (Eq. (12)) because  $\delta\psi$  is an unknown. However, Eq. (24) allows  $\delta\psi$  to be determined: substitution of Eq. (A.2) into Eq. (24) enables us to express  $\delta\psi$  as a function of  $\delta c_j$ , and eliminate it from Eq. (A.2). From here,  $\delta\Gamma_j$  can be easily obtained.

We demonstrate this procedure for the case of strongly charged particles, satisfying Eq. (16). Using Eq. (26a), together with the conditions  $c_3 = (c_1 + c_2)$  and  $\delta c_3 = (\delta c_1 + \delta c_2)$ , it can be shown that:

$$\begin{aligned} \frac{\partial \Gamma_{dj}^0}{\partial \psi_0} &= \text{sign}(\psi_0) \frac{\partial \Gamma_{dj}^0}{\partial |\psi_0|} \approx \text{sign}(\psi_0) \frac{e\Gamma_{dj}^0}{2kT} \\ \frac{\partial \Gamma_{dj}^0}{\partial c_i^0} &= - \frac{\Gamma_{dj}^0}{4(c_1^0 + c_2^0)} \quad i \neq j \\ \frac{\partial \Gamma_{dj}^0}{\partial c_j^0} &= \frac{\Gamma_{dj}^0}{c_j^0} - \frac{\Gamma_{dj}^0}{4(c_1^0 + c_2^0)} \end{aligned} \quad (A.3)$$

Therefore

$$\begin{aligned} \delta\Gamma_{dj} &= \left( \frac{\partial \Gamma_{dj}^0}{\partial \psi_0} \right) \delta\psi + \sum_{i=1}^3 \left( \frac{\partial \Gamma_{dj}^0}{\partial c_i^0} \right) (\delta c_i)_{r=a} \\ &\approx \frac{aR_d}{2} \left[ (\delta c_j)_{r=a} - c_j^0 \delta\psi' - \frac{(-1)^j}{c_1^0 + c_2^0} \right. \\ &\quad \left. \times (\delta c_1 c_{2_0} - \delta c_2 c_{1_0})_{r=a} \right] \quad j=1, 2 \end{aligned} \quad (A.4)$$

where

$$\delta\psi' = -\text{sign}(\psi_0) \frac{e\delta\psi}{kT}$$

As a rule,  $\Gamma_{bj}^0$  are functions of counterion equilibrium concentrations near the particle surface, i.e. they contain factors  $c_j^0 \exp(|y_0|)$ . Hence their

derivatives can be written:

$$\begin{aligned}\frac{\partial \Gamma_{dj}^0}{\partial \psi_0} &= \text{sign}(\psi_0) \frac{ae}{kT} (\beta_{j1} c_1^0 + \beta_{j2} c_2^0) \\ \frac{\partial \Gamma_{bj}^0}{\partial c_i^0} &= a\beta_{ji} \quad i, j = 1, 2 \\ \frac{\partial \Gamma_{bj}^0}{\partial c_3^0} &= 0\end{aligned}\quad (\text{A.5})$$

with

$$\beta_{ji} = \frac{e^{|y_0|}}{a} \frac{\partial \Gamma_{bj}^0}{\partial [c_i^0 \exp(|y_0|)]} \quad (\text{A.6})$$

Hence

$$\begin{aligned}\delta \Gamma_{bj} &= \left( \frac{\partial \Gamma_{bj}^0}{\partial \psi_0} \right) \delta \psi + \sum_{i=1}^3 \left( \frac{\partial \Gamma_{bj}^0}{\partial c_i^0} \right) (\delta c_i)_{r=a} \\ &= a\beta_{j1} [(\delta c_1)_{r=a} - c_1^0 \delta \psi] + a\beta_{j2} [(\delta c_2)_{r=a} - c_2^0 \delta \psi]\end{aligned}\quad (\text{A.7})$$

Substitution of Eq. (A.4) and Eq. (A.7) into Eq. (A.2) yields:

$$\begin{aligned}\delta \Gamma_j &= \delta \Gamma_{dj} + \delta \Gamma_{bj} = \frac{a}{c_1^0 + c_2^0} \\ &\times \{ (-1)^{j+1} (R_d/2) (\delta c_1 c_2^0 - \delta c_2 c_1^0)_{r=a} \\ &+ (R_d/2 + \beta_{jj}) (c_1^0 + c_2^0) + [(\delta c_j)_{r=a} - c_j^0 \delta \psi] \\ &\times \beta_{j,3-j} (c_1^0 + c_2^0) [(\delta c_{3-j})_{r=a} - c_{3-j}^0 \delta \psi] \} \\ j &= 1, 2\end{aligned}\quad (\text{A.8})$$

Substitution of Eq. (A.8) into Eq. (24) gives the following expression for  $\delta \psi'$ :

$$\begin{aligned}\delta \psi' &= \frac{(R_d/2 + \beta_{11} + \beta_{21}) (\delta c_1)_{r=a} \\ &+ (R_d/2 + \beta_{22} + \beta_{12}) (\delta c_2)_{r=a}}{(R_d/2 + \beta_{11} + \beta_{21}) c_1^0 \\ &+ (R_d/2 + \beta_{22} + \beta_{12}) c_2^0}\end{aligned}\quad (\text{A.9})$$

and, after elimination of  $\delta \psi'$  from Eq. (A.8), Eq. (25) for adsorption oscillations is obtained,

with  $R_r$  given by

$$\begin{aligned}R_r &= \frac{R_d}{2} + \frac{(R_d/2 + \beta_{11})(R_d/2 + \beta_{22}) - \beta_{12}\beta_{21}}{(R_d/2 + \beta_{11} + \beta_{21}) c_1^0 / c_3^0 \\ &+ (R_d/2 + \beta_{22} + \beta_{12}) c_2^0 / c_3^0}\end{aligned}\quad (\text{A.10})$$

From this, Eq. (26) can be deduced as a special case: if any  $\Gamma_{bj}^0$  is independent of  $c_{3-j}^0$  (that is,  $\beta_{j,3-j} = 0$ ), we can obtain Eq. (26) by defining the parameters:

$$G_j + \beta_{jj} \geq 0 \quad (\text{A.11})$$

$$\begin{aligned}\gamma &= \frac{-\beta_{12}\beta_{21}}{(R_d/2 + \beta_{11} + \beta_{21}) c_1^0 / c_3^0 \\ &+ (R_d/2 + \beta_{22} + \beta_{12}) c_2^0 / c_3^0}\end{aligned}$$

Eq. (27) and Eq. (28a) are just special cases of Eq. (A.11). The connection between Eq. (29a) and Eq. (A.10) is less trivial. Substitution of the equilibrium adsorption isotherms (Eq. (29)) into Eq. (A.6) yields:

$$\begin{aligned}\beta_{j,3-j} &= -G_{3-j} (c_j^0 / c_j^b) \exp(|y_0|) \\ \beta_{jj} &= G_j - \beta_{3-j,j} \quad j = 1, 2\end{aligned}\quad (\text{A.12})$$

where, from Eq. (29a)

$$G_1 / c_2^b = G_2 / c_1^b \quad (\text{A.13})$$

Substitution of Eq. (A.12) into Eq. (A.10) yields Eq. (26), with

$$\begin{aligned}\gamma &= \frac{G_2 (R_d/2 + G_1) c_1^0 / c_1^b \\ &+ G_1 (R_d/2 + G_2) c_2^0 / c_2^b}{R_d/2 + G_1 c_1^0 / c_3^0 + G_2 c_2^0 / c_3^0} \exp(|y_0|)\end{aligned}\quad (\text{A.14})$$

This equation, together with Eq. (A.13), is equivalent to Eq. (29a) for the parameter  $\gamma$ .

## 7.2. List of main symbols

$a$	particle radius
$c_i$	concentration of ionic species $i$ in the bulk electrolyte
$c_i^0$	equilibrium value of $c_i$
$d_\phi$	induced dipole coefficient (Eq. (7))
$d_{1,2}$	see Eq. (8) and Eq. (9)
$D_{\text{ef},i}$	effective diffusion coefficient (Eq. (11))



$D_i$	diffusion coefficient of the $i$ th ion
$e$	elementary charge
$G_{1,2}$	parameters of $R_F$ (Eq. (26))
$I_j$	tangential flux of the $j$ th ionic species
$J_j$	normal flux of ions of type $j$
$k$	Boltzmann's constant
$K_0$	bulk conductivity
$m_j$	dimensionless parameter of the $j$ th ion
$N$	number of different ionic species in solution
$\mathbf{r}$	position vector with its origin in the particle centre
$r$	modulus of $\mathbf{r}$
$r_{1,2}$	see Eq. (10)
$R_j^{(d,b,v)}$	relaxation parameters of tangential flow of counterion $j$
$R_d$	common value of $R_1^d = R_2^d$
$R_F$	relaxation parameter of counterion adsorption oscillations (Eqs. (25) and (26). High values of $R_F$ mean large adsorption oscillations of counterions)
$T$	absolute temperature
$W_{1,2}$	dimensionless parameters (Eq. (32))
$X$	relative contribution of admixture counterions to the LF limit of the dielectric increment
$y$	dimensionless form of electric potential $\psi$
$y_0$	dimensionless surface potential $\psi_0$
$Z$	relative characteristic frequency
$z_j$	valence of the $j$ th ion
$\Gamma_j$	adsorption density of the $j$ th ion
$\Gamma_j^0$	equilibrium adsorption density of the $j$ th ion
$\Gamma_{dj}^0(\Gamma_{bj}^0)$	equilibrium adsorption density of the $j$ th ions at the diffuse (Stern) layer
$\delta c_i$	contribution of DL polarization to the concentration of the $i$ th ions in the bulk electrolyte
$\Delta \epsilon_r'$	dielectric increment
$\Delta \epsilon_r'(0)$	low-frequency dielectric increment of a colloidal suspension
$\gamma$	parameter of $R_F$
$\delta \psi$	perturbation to the Stern potential at the polarized DL
$\epsilon_0$	permittivity of vacuum
$\epsilon_{rd}'$	Dielectric constant of the dispersion medium

$\zeta$	zeta potential
$\zeta$	dimensionless $\zeta$
$\eta$	viscosity of the dispersion medium
$\theta$	angle between the applied field and the position vector $\mathbf{r}$
$\kappa$	reciprocal Debye length
$\tau_{res}$	mean residence time of adsorbed ions
$\psi$	electric potential in the bulk electrolyte
$\phi$	volume fraction of suspended particles
$\psi_0$	equilibrium Stern potential
$\psi_0$	dimensionless form of $\psi_0$
$\omega$	frequency of the applied AC field
$\omega_{cr}$	characteristic relaxation frequency

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